REMARKS

Reconsideration of this application is respectfully requested in view of the foregoing amendments and the following remarks.

Claims 1 and 3 of the present application stand rejected under 35 USC §103(a) as being obvious over Martin et al. (No. 3,978,315) in view of Alexander (No. 3,110,571) or Flaitz et al. (No. 4,764,341). Claim 2 stands rejected under 35 USC §103(a) as being obvious as described above and further in view of Strange (No. 5,728,638).

Claims 4, 5, 9-13, 17 and 19 stand rejected under 35 USC §102(b) as being anticipated by Martin et al. And Claims 6-8 and 14-16 stand rejected under 35 USC §103(a) as being obvious over Martin et al. in view of Strange et al., or Rousset et al. (No. 5,462,903), or Howard et al. (No. 5,227,345).

In response to Applicants' arguments filed August 27, 2004, the Examiner has observed that Applicants' assertion that the applied prior art does not teach the forming of certain of the defined layers by thermal spraying is misplaced since the claims are directed to an apparatus and not to a method or process. By this response Applicants have corrected this deficiency by amending the claims to expressly recite that certain of the defined layers have a "thermally sprayed structure." In particular, the process of forming a layer by thermal spraying not only results in better adhesion, but also produces a structure that is uniquely identifiable. As demonstrated by the attached two publications (which were obtained from the internet links noted on the publications), a thermally sprayed layer comprises a plurality of "splats" that are formed by the high velocity impact of the at least partially molten or liquefied particles or droplets when

impacting onto the respective surface. Thus, one of ordinary skill in the art understands the unique structure that results from the formation of a thermally sprayed layer.

Contrary to the Examiner's position, the primary reference to Martin et al. does not teach or suggest a thermally sprayed structure. At column 6, lines 30-39, Martin et al. states:

> "The most convenient method of providing a coating of the glass on a glass-ceramic plate is to provide a paste or slurry of powdered glass in a suitable oil vehicle, and then to apply the glass-containing paste of slurry to the plate by brushing, spraying, silk-screening, doctor blading or other conventional techniques. The resulting coating is then fired to remove the binder, sinter and bond the glass to the plate, and crystallize the glass to provide the desired semicrystalline layer."

Accordingly, Martin et al. merely discloses that a paste or slurry of powdered glass in a suitable oil vehicle may be provided and then applied to the plate by brushing, spraying, silk-screening, doctor blading or other conventional techniques. Thereafter, the resulting coating is fired to remove the binder, sinter and bond the glass to the plate, and crystallize the glass to provide the desired semi-crystalline layer. However, the "spraying" disclosed in this regard produces a completely different structure than the "thermal spraying structure" currently claimed in this application. A paste or slurry contained in a suitable oil vehicle can only be sprayed in cold condition at room temperature.

By contrast, the claimed "thermal spraying structure" is achieved by a completely different technology according to which the powdered material is thermally sprayed at extremely high temperatures up to 2000 or 3000°C under the influence of extreme heat generation, such as by a plasma spray gun. Nothing in Martin et al. can be read to suggest a thermal spraying structure as currently claimed.

Accordingly, the claims as now presented are believed to patentably distinguish over the cited art. Favorable reconsideration is respectfully solicited.

Respectfully submitted,

Dated: February 25, 2005

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Thermal Spray Coatings

Contents: Bonding, Coating structure, Stress, Properties, Porosity, Oxide, Surface texture, Strength, NDT, Process factors, Links

Nature of Thermal Spray Coatings

What is a thermal (flame) spray coating? A coating produced by a process in which molten or softened particles are applied by impact onto a substrate.

A common feature of all thermal spray coatings is their lenticular or lamellar grain structure resulting from the rapid solidification of small globules, flattened from striking a cold surface at high velocities.

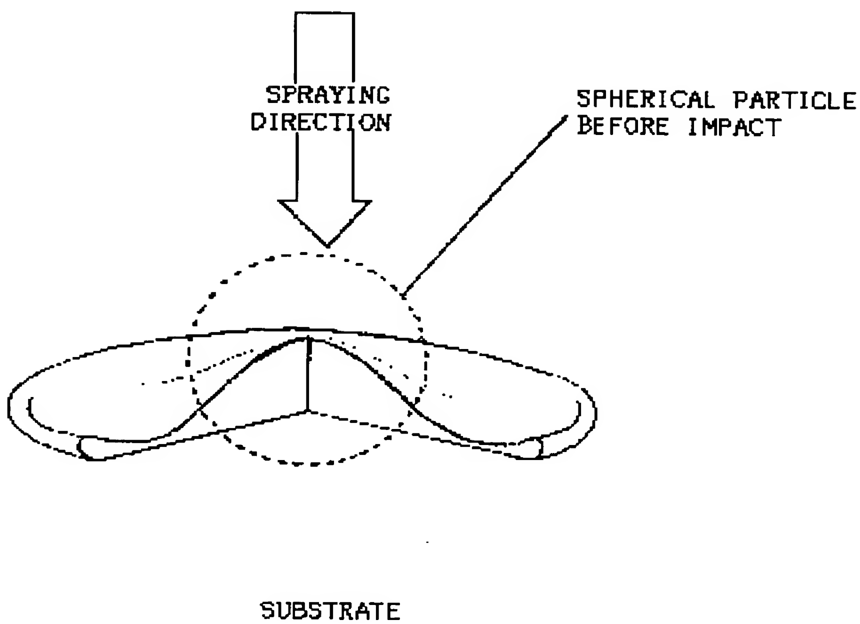
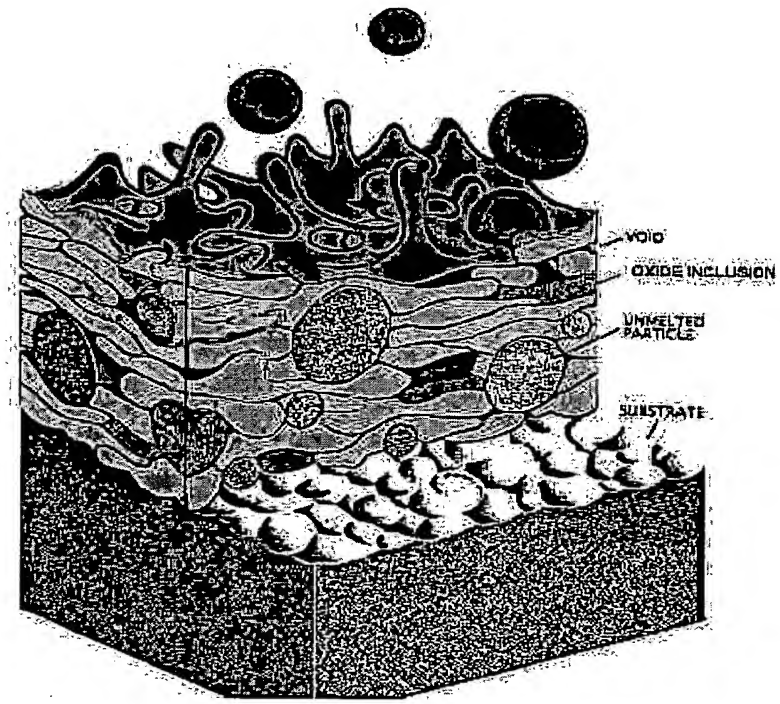


Fig.1 Schematic diagram of thermally sprayed spherical particle impinged onto a flat substrate



Schematic Diagram of Thermal Spray Metal Coating

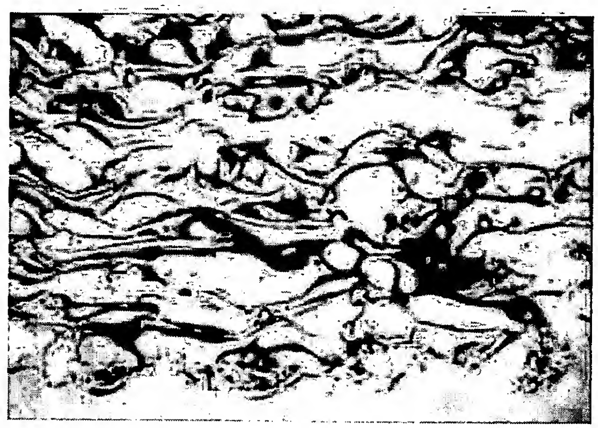


Fig.2. A typical microstructure of a metallic thermally sprayed coating. The lamellar structure is interspersed with oxide inclusions and porosity.

Links to other Photomicrographs: *Plasma Sprayed Coatings* / *Plasma Sprayed Chromium Oxide Coatings 1* * *Plasma Sprayed Chromium Oxide Coatings 2* **Combustion Thermal Sprayed Coatings* / *HVOF Thermal Spray Coatings* / *Plasma Spray WC/Co* / *WC/NiCrBSi* / *Rogues Gallery* / *Thermal spraying onto Composite Substrates* / Effect of Metallographic Preparation Technique on Thermal Spray Coatings

BONDING. *back to contents)*

The bonding mechanisms at the thermal spray coating/substrate interface and between the particles making up the thermal spray coating is an area which in many cases is still subject to speculation. It generally suffices to state that both mechanical interlocking and diffusion bonding occur.

Thermal Spray Coating Bonding Mechanisms:

- Mechanical keying or interlocking.
- Diffusion bonding or Metallurgical bonding.
- Other adhesive, chemical and physical bonding mechanisms -oxide films, Van der Waals forces etc.

Factors effecting bonding and subsequent build up of the coating:

- Cleanliness
- Surface area
- Surface topography or profile
- Temperature (thermal energy)
- Time (reaction rates & cooling rates etc.)
- Velocity (kinetic energy)
- Physical & chemical properties
- Physical & chemical reactions

Cleaning and grit blasting are important for substrate preparation. This provides a more chemically and physically active surface needed for good bonding. The surface area is increased which will increase the coating bond strength. The rough surface profile will promote mechanical keying.

Individual particle cooling rates on impact can be of the order of 1 million ° C per second ($10^6 Ks^{-1}$). Thermal interaction is obviously very limited. Important with regard to diffusion bonding (temperature and time dependent).

Increase in thermal and kinetic energy increases chances of metallurgical bonding. (temperature, velocity, enthalpy, mass, density an specific heat content etc.). Thermal spray materials like Molybdenum, Tungsten, and Aluminium / metal composites produce so called "self bonding" coatings. These materials have comparatively high bond strengths (increased metallurgical or diffusion bonding) and can bond to clean polished substrates

Molybdenum and other refractory metals have very high melting points thus the interaction between substrate and coating particles will be increased due to the higher temperatures involved and longer cooling cycles. Also molybdenum oxide volatilizes and does not get in the way of metallurgical bonding.

Aluminium / metal composites produce increased levels of exothermic reaction due to reactions of aluminium with metals like nickel to produce nickel aluminide and with oxygen producing aluminium oxide. The increased thermal action increases degree of diffusion bonding.

Higher preheat temperatures for the substrate increase diffusion bonding activities but will also increase oxidation of the substrate which could defeat the objective of higher bond strengths.

High kinetic energy thermal spraying using HEP, HVOF and cold spray produce high bond strengths due to the energy liberated from high velocity impacts. The high density tungsten carbide/cobalt and cold spray coatings are good examples.

Metallurgical or diffusion bonding occurs on a limited scale and to a very limited thickness (0.5 μm max. with heat effected zone @ 25μm) with the above type coatings.

Fused coatings are different. These are remelted and completely metallurgically bonded with the substrate and its self.

COATING STRUCTURE

(back to contents)

High cooling rates or super cooling (10^6 Ks^{-1}) of particles can cause the formation of unusual amorphous (glassy metals) microcrystaline and metastable phases not normally found in wrought or cast materials.

A large proportion of thermal spraying is conducted in air or uses air for atomisation. Chemical interactions occur during spraying, notably oxidation. Metallic particles oxidize over their surface forming an oxide shell. This is evident in the coating microstructure as oxide inclusions outlining the grain or particle boundaries. Some materials (such as titanium) interact with or absorb other gases such as hydrogen and nitrogen.

Coatings show lamellar or flattened grains appearing to flow parallel to the substrate. The structure is not isotropic, with physical properties being different parallel to substrate (longitudinal) than across the coating thickness (transverse). Strength in the longitudinal direction can be 5 to 10 times that of the transverse direction.

The coating structure is heterogeneous relative to wrought and cast materials. This is due to variations in the condition of the individual particles on impact. It is virtually impossible to ensure that all particles are the exact same size and achieve the same temperature and velocity.

All conventionally thermally sprayed coatings contain some porosity (0.025% to 50%). Porosity is caused by:

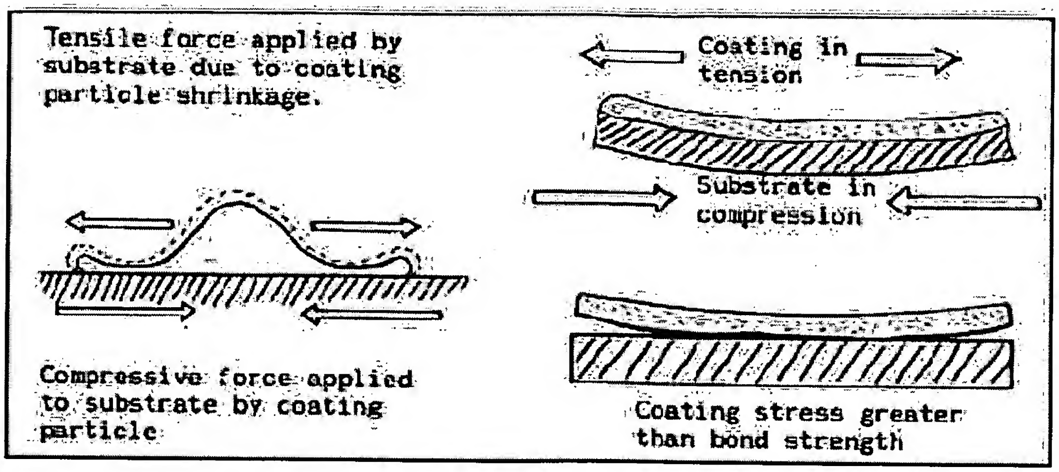
- Low impact energy (unmelted particles / low velocity)
- Shadowing effects (unmelted particles / spray angle)
- Shrinkage and stress relieve effects

The above interactions can make the coatings very different from their starting materials chemically and physically.

STRESS

(back to contents)

Cooling and solidification of most materials is accompanied by contraction or shrinkage. As particles strike they rapidly cool and solidify. This generates a tensile stress within the particle and a compressive stress within the surface of the substrate. As the coating is built up, so are the tensile stresses in the coating. With a lot of coatings a thickness will be reached where the tensile stresses will exceed that of the bond strength or cohesive strength and coating failure will occur.



High shrink materials like some austenitic stainless steels are prone to high levels of stress build up and thus have low thickness limitations. Look out for thickness limitation information on coating data sheets. Generally thin coatings are more durable than thick coatings.

Spraying method and coating microstructure influence the level of stress build up in coatings. Dense coatings are generally more stressed than porous coatings. Notice that Combustion powder sprayed coatings generally have greater thickness limitations than plasma coatings.

Contrary to that just mentioned, the systems using very high kinetic energy and low thermal energy (HVOF, HEP, cold spray) can produce relatively stress free coatings that are extremely dense. This is thought to be due to compressive stresses formed from mechanical deformation (similar to shot peening) during particle impact counteracting the tensile shrinkage stresses caused by solidification and cooling.

PROPERTIES

(back to contents)

Compare coatings to their wrought or cast equivalents:

PROPERTY	COATING	CAST/WROUGHT
Strength	low (5-30%)	100%
Ductility	very low (1-10%)	100%
Impact	low	high
Porosity	yes (not if fused)	in some castings
Hardness	slightly higher (microhardness)	
Wear resistance	high	low
Corrosion	low resistance	high resistance
Machining	poor	good

This comparison generally shows coating properties in a bad light, and does not take into consideration that coatings are usually supported by a substrate. Coatings are generally only used to give surface properties such as wear resistance and not to add strength.

Remember, bulk strength supplied by the substrate (cheap, strong and ductile). Surface properties supplied by the coating (wear and corrosion, etc.). Due to the small quantity of material required for a coating, more exotic materials can be used economically. The properties of some coatings cannot be fabricated by any other method.

Properties of coatings should be considered in their own right and not the properties of the original material prior to spraying as they can be very different physically and chemically.

Porosity

(back to contents)

This is present in most thermally sprayed coatings(except VPS, post heat treated coatings or fused coatings). 1 to 25% porosity is normal but can be further manipulated by changes in process and materials.

Porosity can be detrimental in coatings with respect to:

- Corrosion - (sealing of coatings advised).
- Machined finish.
- Strength, macrohardness and wear characteristics.

Porosity can be important with respect to:

- Lubrication - porosity acts as reservoir for lubricants.
- Increasing thermal barrier properties.
- Reducing stress levels and increasing thickness limitations.
- Increasing shock resisting properties.
- Abradability in clearance control coatings.
- Applications in prosthetic devices and nucleate boiling etc.

Oxide

(back to contents)

Most metallic coatings suffer oxidation during normal thermal spraying in air. The products of oxidation are usually included in the coating. Oxides are generally much harder than the parent metal. Coatings of high oxide content are usually harder and more wear resistant. Oxides in coatings can be detrimental towards corrosion, strength and machinability properties.

Surface Texture

(back to contents)

Generally the as-sprayed surface is rough and textured. The rough and high bond strength coatings are ideal for bond coats for less strongly bonding coatings. Many coatings have high friction surfaces as-sprayed and this property is made use of in many applications (rolling road drum surfaces for MOT brake testing). Some plasma sprayed ceramic coatings produce smooth but textured coatings important in the textile industry. Other applications make use of the abrasive nature of some coating surfaces. Thermally sprayed coatings do not provide bright high finish coatings with out finishing like that of

electroplated deposits.

Strength

(back to contents)

Coatings generally have poor strength, ductility and impact properties. These properties tend to be dictated by the "weakest link in the chain" which in coatings tends to be the particle or grain boundaries and coating/substrate interface. Coatings are limited to the load they can carry, and thus require a substrate for support, even then, coatings are poor when point loaded.

Internal tensile coating stresses generally adversely effect properties. Effective bond strength is reduced and can be destroyed by increasing levels of internal stress. This in turn effects coating thickness limits. Coatings on external diameters can be built up to greater thickness than that on internal diameters.

Surface properties such as wear resistance are usually good, but the properties are more specific to the material or materials used in the coating. The properties of a substrate need only to be strength, ease of fabrication and economic (like mild steel). The coating supplies the specific surface properties desired. For example, materials used for applications of thermal barrier and abradable clearance control by nature have poor strength and thus benefit from being applied as a coating onto a substrate which supplies the strength.

Some Properties Thermally Sprayed Coatings can Provide:

- Tribological (wear, resistance).
- Corrosion resistance.
- Heat resistance.
- Thermal barrier.
- Electrical conductivity or resistivity
- Abradable or abrasive.
- Textured surfaces.
- Catalyst and prosthetic properties,
- Restoration of dimension.
- Copying of intricate surfaces.

(back to contents)

NON-DESTRUCTIVE TESTING OF THERMALLY SPRAYED COATINGS.

There are very few reliable NDT methods available for thermally sprayed coatings. The majority of tests for coatings tends to be of a destructive nature, which, obviously can not be used on the actual coated part going into service and therefore, must be considered as a test for process control.

The main practical NDT methods used are:

- Dimensional measurements- micrometer, eddy current and magnetic thickness measuring devices etc.

- Machining tests-response of coating during machining operations is a good test for general integrity.

- Visual inspection- grit blast, spraying, coating/substrate, machined finish.
- Dye penetrant- used in limited applications, but natural coating porosity fogs flaw indications.

Ultrasonic and magnetic particle flaw detection methods have proved to be poor with thermally sprayed coatings due to the very high number of particle boundaries giving flaw like responses and causing high levels of interference.

Hardness testing is generally considered a destructive test for coatings unless made in a non-working area.

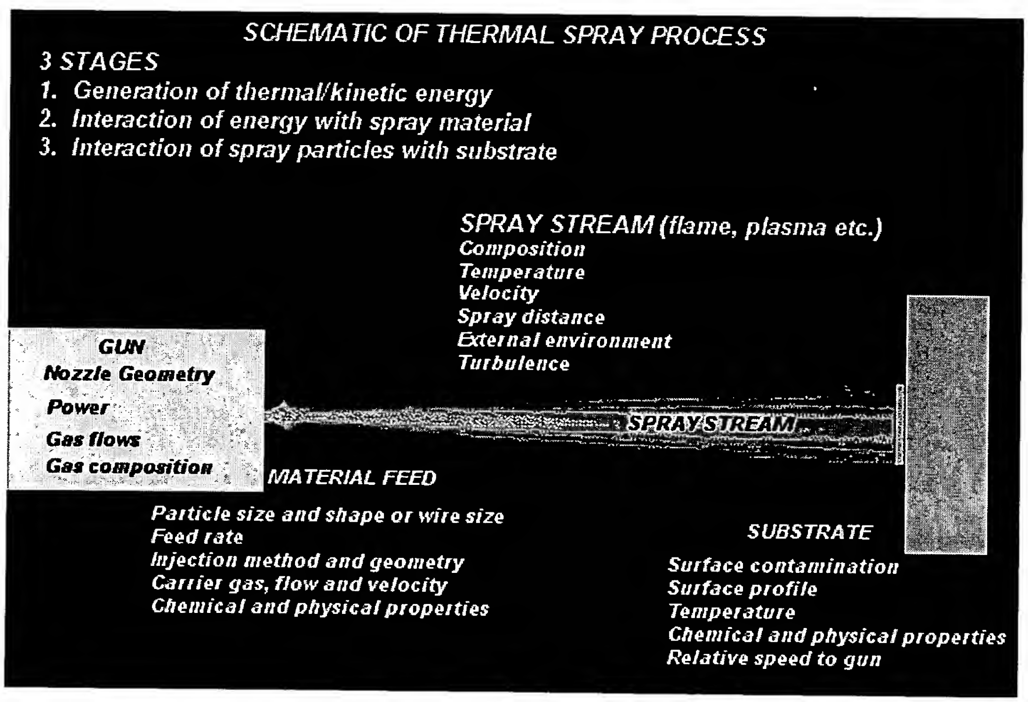
Advanced techniques like thermography, Thermal wave interferometry and acoustic emission are presently being researched and are still laboratory set-ups with limited practical use for industry.

Destructive testing such as hardness, bend, bond strength, metallography etc. are important to prove the process and coating integrity expected in the component.

The limited non-destructive testing available for thermally sprayed coatings should emphasise the need for a high standard of quality control over the process, to ensure a high level of confidence in the coated products.

(back to contents)

Factors Effecting The Thermal Spray Coating Process



(back to contents)

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THERMAL SPRAY COATING PAGE INDEX

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Thermal Spraying – An Overview

Topics Covered

Background

The demands for engineering coatings are becoming more and more stringent. Environmental concerns are also being considered as an integral part of the design process. For future economic competitiveness and a lower environmental impact we must therefore turn our attention to processes that use the minimum of resources. Thermal spraying is an attractive coating technique as it offers a wide choice of materials and processes that have a reduced impact on the environment when compared to conventional plating processes.

Thermal spray coating techniques such as flame spraying, wire arc spraying and plasma spraying, allow many problems of wear, corrosion and thermal degradation to be resolved by engineering the surface with tailor-made coatings. For example, turbines can be coated by thermally spraying, allowing their use at higher temperatures.

How does Thermal Spraying Work?

In the thermal spraying process, heated and melted particles are propelled towards a substrate where they are flattened and quenched very rapidly. A thermal

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sprayed coating consists of layers of splats which have a lamellar cross section. Typically the cooling rate of each splat is somewhere in the vicinity of one million degrees per second. This rapidly quenched microstructure can have unique characteristics quite unlike those produced by conventional processing techniques e.g. the extension of solid state solubility, refinement of grain size, formation of metastable phases and a high concentration of point defects.

Variations of Thermal Spraying

There are many variations of thermal spraying technology. In flame spraying the combustion of a fuel gas is used to heat the material. In atmospheric plasma spraying (APS) the material is melted and accelerated in a plasma jet. To avoid oxidation of the feed material, spraying can be carried out in an inert gas atmosphere, at a reduced pressure (known as vacuum plasma spraying VPS or low pressure plasma spraying LPPS). In high velocity oxy-fuel spraying (HVOF), material is injected into a high velocity jet generated by burning a fuel mixed with oxygen at high pressure.

Advantages of Thermal Spraying

Compared to traditional surface modification processes, thermal spraying offers greater thickness capability, no part size restrictions, it can be performed in situ, and it produces minimal noxious waste. High processing temperatures allow deposition of many high melting point materials onto a relatively cold substrate.

Applications and the Market

Thermally sprayed coatings have, in recent years, gained wide spread acceptance for a variety of industrial applications - the global market for thermal sprayed coatings is currently about $1.35 billion. This growth has been primarily technology led, and high value plasma coatings hold the lion's share of the market. A vast majority of these applications involve wear resistance, although the use of thermal sprayed coatings in combating high temperature corrosion also continues to receive considerable industrial and academic interest. These sprayed coatings are applied in order to achieve predeterminable life periods under severe operating conditions. For example, thermal sprayed coatings have been used extensively to prevent stress corrosion cracking in high strength low alloy steels used for liquid petroleum gas tanks. Other surface properties and functions that thermally sprayed coatings can provide are, biological compatibility, electrical resistance/conductivity, thermal barriers, and dimensional restoration.

Extensive use of thermal spray technology has been

instrumental in Europe attaining worldwide leadership in the paper and textile industry. Pioneering applications of thermally sprayed wear resistant coatings to blades, rolls and looms have allowed a significant increase in production rates. The aeronautic and space industries have also benefited considerably - many components in modern aircraft depend on hard, wear resistant coatings which can withstand temperatures of about 850°C. This type of application represents approximately 40% of the total market.

Surface Protection

Surface protection at high temperatures has become one of the most advanced fields of modern engineering. Diverse examples include rocket thrust chamber linings, chemical reaction vessels, combustion vanes and land-based turbines for aircraft, and hot extrusion dies. These coatings usually consist of carefully selected ceramic and metal layers which provide adequate thermal fatigue resistance and corrosion protection. The use of protective coatings for corrosion prevention has grown rapidly during the past decade, and thermal spray coatings represent a significant portion of this growth.

Microelectronics

Thermal sprayed coatings can also be used to manufacture hybrid microelectronic components, by spraying ceramic materials onto a metal substrate to provide electrically insulating areas. Such technology is becoming increasingly important in meeting the demands of modern computing.

Biomaterials

Biomaterials account for about 41% of the total weight of thermal sprayed materials in the world. Biomedical requirements in prostheses are complex and diverse in nature. Often, a combination of coating materials is needed to suit the various stages of the bio-integration process of foreign material into the human body. Functionally graded bioceramic coatings are used to enhance both the biocompatability and corrosion resistance of implants.

Mechanical Properties

The mechanical properties of coatings depend strongly on their microstructure and especially on the porosity and the interlamellar contacts. These depend heavily on the consumables used and the processing route used. Hardness is one of the key properties of a thermally sprayed coating, as this is often used to give a first approximation of coating wear resistance. Measurements of hardness also allow a quick estimation

of coating strength and the quality of spraying, because specific processing defects, such as porosity and unmelted grains, can lower coating hardness.

Wear Resistant Coatings

Carbides and oxides are the hardest thermal sprayed coatings, the most commonly sprayed being WC-Co cermets. Cermet and ceramic coatings are therefore the most suitable for wear applications. The elastic moduli of the A13S sprayed coatings are significantly less than the bulk material. Carbides and oxides typically have a modulus which is 20-30% of the bulk value, though this value is heavily dependent on the processing route. Sprayed metal coatings generally have a modulus of about 30% of the bulk value, although this may be comparable with the bulk properties for coatings produced using the LLPS system.

Thermal Barrier Coatings

Thermal barrier coatings (TBCs) depend on low thermal conductivity and thermal diffusivity. The state-of-the-art TBC system at the moment is an air plasma sprayed $Zr0_2$/6-8wt% Y_20_3 ceramic layer over a NiCrAlY bond coat layer, deposited by plasma spraying at low pressure. Partially stabilised zirconia has been chosen as the top coat because of its excellent thermal shock resistance, low thermal conductivity and relatively high coefficient of thermal expansion. The thermal conductivity and strain tolerance is further enhanced by the microcrack network, figure 1, produced in the individual splats due to spraying.

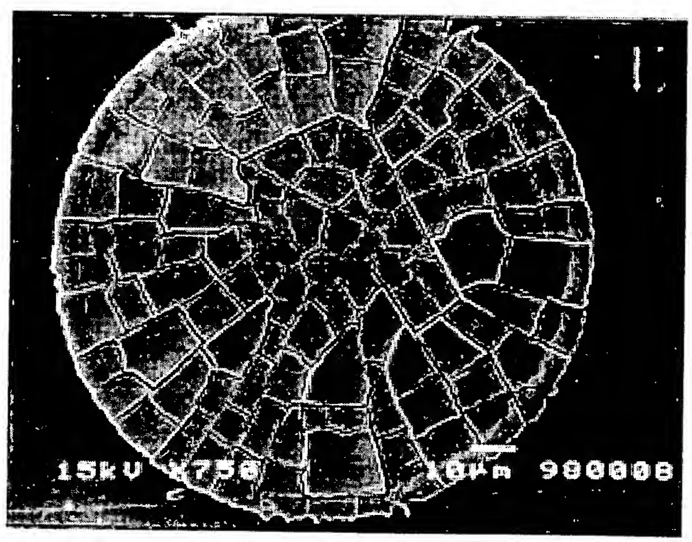

Figure1. A typical plasma sprayed ceramic splat showing network of microcracks.

The Future

In the future the manufacturing and engineering industries will continue to change dramatically, and for numerous engineering or consumer durable products appropriate surface engineering as applied by thermal spraying techniques is becoming a decisive factor in sustaining a competitive edge.

Among the many surface engineering techniques available, thermal spray techniques are particularly well placed to meet the market demands. They allow the manufacture of a large variety of coatings, deposition of elaborate multimaterials (such as functionally gradient coatings) and offer a great potential for the development of new innovative coatings which can be processed with the minimal environmental disturbance.

HVOF

HVOF is expected to increase its share of the market significantly - hard cermet coatings are increasingly replacing conventional chrome plating, and oxidation resistant alloy coatings for turbine engines, which were sprayed exclusively by LPPS, are now also produced by HVOF. This is because the technique can produce very dense coatings with reduced oxidation and decomposition of the feed materials in air.

Barrier Coatings

One of the most challenging goals for thermal spray technology is barrier-type coatings for corrosion resistance, because almost complete removal of through-porosity is required. VPS has been successful to some extent, but if such coatings could be made in air, a greater number of applications could be realised. To achieve this aim, improvements are being made to APS as well as HVOF processes by introducing a gas shroud or laser skin melting.

Corrosion/Wear Coatings

Ceramic coatings also merit greater consideration for applications involving corrosion plus wear. However, it is important that as much care is given to selection of the bond coat as to the ceramic coating if these coatings are to perform as well as anticipated.

Conclusion

Another possible route for improving ceramic coatings would be to take advantage of the new wave of structural ceramics. Approaches such as fibre loading and controlled and reaction toughening could yield significant improvements in coating response.

Thermal sprayed coatings may not be the answer to every problem involving surface degradation of a component, they are just one weapon in an arsenal.

However, the technique does offer a great range of coating operations, and provides an appealing opportunity for innovation, while putting less pressure on environmental resources.

Primary author: Dr. Philip Blazdell and Dr. Seiji Kuroda
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top

back